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THE FRACTURE TOUGHNESS OF EPOXY-GLASS BEAD COMPOSITES

BY

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JANUARY 1971

FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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THE FRACTURE TOUGHNESS OF EPOXY-GLASS BEAD
COMPOSITES

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Abstract

The plane strain fracture toughness of epoxy resins and glass bead filled epoxy composites has been investigated. Primary parameters were curing agent concentration, filler concentration, adhesion of filler to polymer, temperature, and water immersion. Fracture toughness was measured using double edge notched specimens and tensile strength and Young's modulus were measured using standard ASTM tensile bars. Scanning electron microscopy was used to examine the fracture surfaces.

It was found that the energy required for fracture depended primarily on the ability to dissipate energy in the polymer phase. At higher temperatures and/or increased catalyst concentration, the unfilled epoxy became more ductile, its fracture surface became rougher, and its fracture energy was increased. At lower temperatures, where the epoxy was relatively brittle, the addition of glass beads increased the fracture energy and induced roughness in the otherwise smooth fracture surface. When the epoxy was ductile, the addition of beads tended to decrease the fracture energy. The reduction of fracture energy for the ductile polymer was attributed to the reduction

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of the amount of polymer surface created.

Adhesion of the matrix to the glass beads was only important when the polymer was ductile. Improved adhesion permitted the beads to constrain polymer flow and decrease the fracture energy. Poor adhesion permitted flow around the beads which required additional energy for crack propagation. At low temperatures, where the matrix was brittle, the additional constraints caused by adhesion appeared to make little difference.

Water absorption resulted in plasticizing the polymer, destroying the interface, and probably destroying the polymer near the interface. Short term immersion increased the toughness because of the additional ductility. Long term immersion tended to reduce the toughness. An effective coupling agent minimized this reduction, thereby showing that improved adhesion can improve the environmental stability and extend the useful life of the material.

THE FRACTURE TOUGHNESS OF EPOXY-GLASS BEAD COMPOSITES

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Introduction

The fracture toughness of glass bead-epoxy composites depends primarily on the ability to dissipate energy in the polymer phase. Factors which enhance polymer flow and/or polymer surface roughness also increase the fracture toughness. The parameters investigated included glass bead concentration, temperature, adhesion of polymer to filler, water immersion, and curing agent concentration. The fracture toughness was measured using double edge notched tensile specimens as described previously (1).

The fracture toughness parameter (γ) is defined by Irwin (2) as:

$$\gamma = \frac{\sigma^2 W(1 - \nu^2)}{2E} \left[\tan \frac{\pi (a + r_y)}{W} + 0.1 \sin \frac{2\pi (a + r_y)}{W} \right]$$

where σ is the gross section stress at onset of catastrophic fracture, based on the original cross-section, W is the sample width, E is Young's modulus, ν is Poisson's ratio, a is the half crack length at onset of catastrophic fracture, and r_y is Irwin's plastic zone correction factor, given by:

$$r_y = \frac{\gamma E}{\pi (1 - \nu^2) \sigma_y^2}$$

where σ_y is the yield strength of the material.

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The Poisson's ratio for a composite was computed by the rule of mixtures, (i.e., a volume fraction average) with $\nu = 0.35$ for the epoxy and $\nu = 0.22$ for the glass beads.

The glass beads were Class IV Uni-Spheres, number 4000, diameter range of 1 to 30 microns, purchased from Microbead Division, Cataphote Corporation. To enhance adhesion, the beads were treated with either Union Carbide's A-1100 (gamma-aminopropyltriethoxysilane) or A-187 (gamma-glycidoxypropyltrimethoxy-silane). To prevent adhesion, the beads were treated with Union Carbide's A-156 (dimethyldichlorosilane). Beads left untreated were used for a fourth composite system.

The resin used was Shell's Epon 828, a diglycidyl ether-bisphenol A type epoxy. The curing agent was Curing Agent Z, a liquid eutectic mixture of aromatic amines. The curing cycle for the systems was 24 hours at room temperature, 24 hours at 60°C, 24 hours at 100°C, and 12 hours at 130°C, followed by slow cooling. The samples were machined, further conditioned by annealing at 100°C for 12 hours and then stored in desiccators over silica gel until testing. The specimens used for the water immersion studies were immersed in distilled water at room temperature for the specified time.

Results

Fracture toughness of the Epon 828/Curing Agent Z epoxies appeared to depend solely on the ability to dissipate energy in the polymer phase. The results for the dry epoxies are summarized in Table 1. The effects of immersing these samples in water are detailed in Table 2. The postulated explanations of the observed phenomena are

based primarily on scanning electron microscope photographs of the fracture
surfaces, tensile strengths and Young's moduli.

Increase in the curing agent concentration or temperature increased the
fracture toughness of unfilled epoxy as shown in Figure 1. Apparently, incompletely
reacted curing agent served as plasticizer and thereby lowered the glass transition
temperature and enhanced viscous flow during fracture. Similarly, higher tempera-
tures caused a corresponding enhancement of ductility and polymer flow, and thus
increased the fracture toughness. These increases in ductility were apparent in the
fracture surface morphology as illustrated in Figures 2 and 3. The increase in
temperature had a greater effect on increasing the surface roughness than did the
increase in curing agent concentration. Further evidence of the increased ductility
is shown by the decrease in Young's modulus (Figure 4) and the decrease in tensile
strength (Figure 5).

Addition of glass beads to the brittle epoxy (Epon 828/20 phrZ) resulted in
increased fracture toughness at room temperature as shown in Figure 6. As is evident
from comparing Figure 7 with 2, the addition of beads resulted in increased roughness
in the fracture surface, and probably increased the total amount of polymer surface per
unit area of cross-section. This additional polymer surface was probably instrumental
in increasing the fracture toughness. Only insignificant changes due to glass bead
surface treatment were observed at room temperature.

At 100°C and 130°C (illustrated for 130°C in Figure 8), the fracture toughness
of A-156 silane treated beads was significantly greater than the fracture toughness of
the other epoxy composites. A close examination of the fracture surfaces reveals

that when there is no adhesion, the polymer tends to flow away from the filler inter-
face leaving a large smooth crater within which the particle sits (Figure 9). On the
other hand, when there is adhesion, the polymer tends to be constrained by the rigid
filler surface and in a region of about 1/4 to 1/2 micron around the filler surface there
is a tendency for cavitation of the polymer rather than gross yielding (Figure 10). The
same situation exists in PPO-glass composites (1), but to even a greater extent. The
constraint to flow and the supplanting of the polymer by the addition of beads are
probably the primary factors that cause the decrease of the fracture toughness for
these composites. The tensile strengths and Young's moduli are illustrated in Figures 11
and 12. Below the glass transition temperature Young's modulus was not affected by
bead surface treatment.

The fracture toughness of the unfilled epoxy increased significantly upon short
term immersion in distilled water at room temperature (Figure 13). Similar increases
for untreated bead composites after 100 hours are shown in Table 2. However, after
135-160 days in water, the fracture toughness of untreated and A-156 treated materials
reverted to slightly lower values than the dry composites. The fracture toughness for
composites containing A-1100 silane treated glass beads continued to increase for
longer periods of time as shown in Table 2 but ultimately reached a fairly constant
value. In all cases the water immersion caused decreases in tensile strength ranging
from 20 to 50 percent of the dry strength.

The amount of water absorbed per unit volume of polymer in the composites
is shown in Figure 14. For immersions of the order of 135-160 days, the amounts of
water absorbed per unit volume of polymer was greater than for the unfilled polymer
when there was no adhesion between polymer and filler (A-156) but was less than for
the unfilled polymer when there was good adhesion (A-1100). This clearly suggests

that water accumulated at the poorly bonded interfaces causing a destruction of the interface and a decrease in the physical properties of the system. Good adhesion at the interface, however, caused a barrier to migration of water and in fact promoted a lowering of the solubility of water in the epoxy near the interface, thereby at least temporarily protecting the hydrophilic surfaces from damage.

The tentative explanation for the initial increase in toughness and continual decrease in strength is that the polymer phase is slightly plasticized during the initial stage of water sorption, thereby enhancing the ductility. Continued sorption, however, leads to a migration of the water to the hydrophilic glass surfaces thus causing a degradation of all physical properties. The development of good adhesion at the interface retards this latter phenomenon, thereby extending the useful life and improving the environmental stability of the material.

It is the opinion of the authors, however, based on tentative data that will be reported at a later date, that improved adhesion merely retards the migration of water to the interface and that longer term exposure of these systems leads to the same kind of degradation observed in the poorly adhering systems.

Acknowledgemsnt

References

1. A. Wambach, K. Trachte, and A. DiBenedetto, "Fracture Properties of Glass Filled Polyphenylene Oxide Composites," J. of Composite Materials, Vol. 2, No. 3, (266) (July 1968).

2. G. R. Irwin, "Fracture Toughness Testing of High-Strength Sheet Materials under Conditions Appropriate for Stress Analysis." Naval Research Laboratory Report No. 5846 (1960).

TABLE 1.

Summary of Fracture Toughness Data for Dry Epoxy Systems.

Material	Parameter	Effect on γ of increase in Parameter	Reason	Evidence
Unfilled Epoxy	Curing Agent Concentration	Increase	Incompletely reacted curing agent plasticized epoxy	Decrease in strength and modulus, increase in fracture surface roughness
Unfilled Epoxy	Temperature	Increase	Increase in ductility	Decrease in strength and modulus; increase in fracture surface roughness
Glass Bead/ Epoxy Composites at 25°C	Adhesion	None	Constraints on polymer flow due to adhesion are not important when polymer is very brittle	Fractographic plus toughness data
Glass Bead/ Epoxy Composites at 100°C, and 130°C	Adhesion	Decrease	Adhesion at interface constrains polymer flow and significantly reduces energy absorbing ability of polymer.	Fractographic plus toughness data.

TABLE 1 - Continued

Material	Parameter	Effect of γ on increase in Parameter	Reason	Evidence
A-156 Silane treated Glass Bead/Epoxy Composites at 25°C, 100°C and 130°C	Glass Bead Concentration	Increase	Increase in total polymer fracture surface due to increased roughness plus unconstrained polymer flow around beads at fracture surface.	Fractographic
Untreated, A-1100 silane treated, and A-187 silane treated Glass Bead/Epoxy Composites at 25°C	Glass Bead Concentration	Increase	Increase in polymer fracture surface roughness counterbalances the supplanting of polymer by beads. Polymer ductility is not a dominant factor.	Fractographic
Untreated, A-1100 silane treated and A-187 silane treated Glass Bead/Epoxy Composites at 100°C and 130°C.	Glass Bead Concentration	Decrease	Increase in total polymer fracture surface is counter-acted by constraint of polymer flow near beads.	Fractographic

TABLE 2

Effect of Water Immersion on Fracture Toughness
of Epoxy Systems

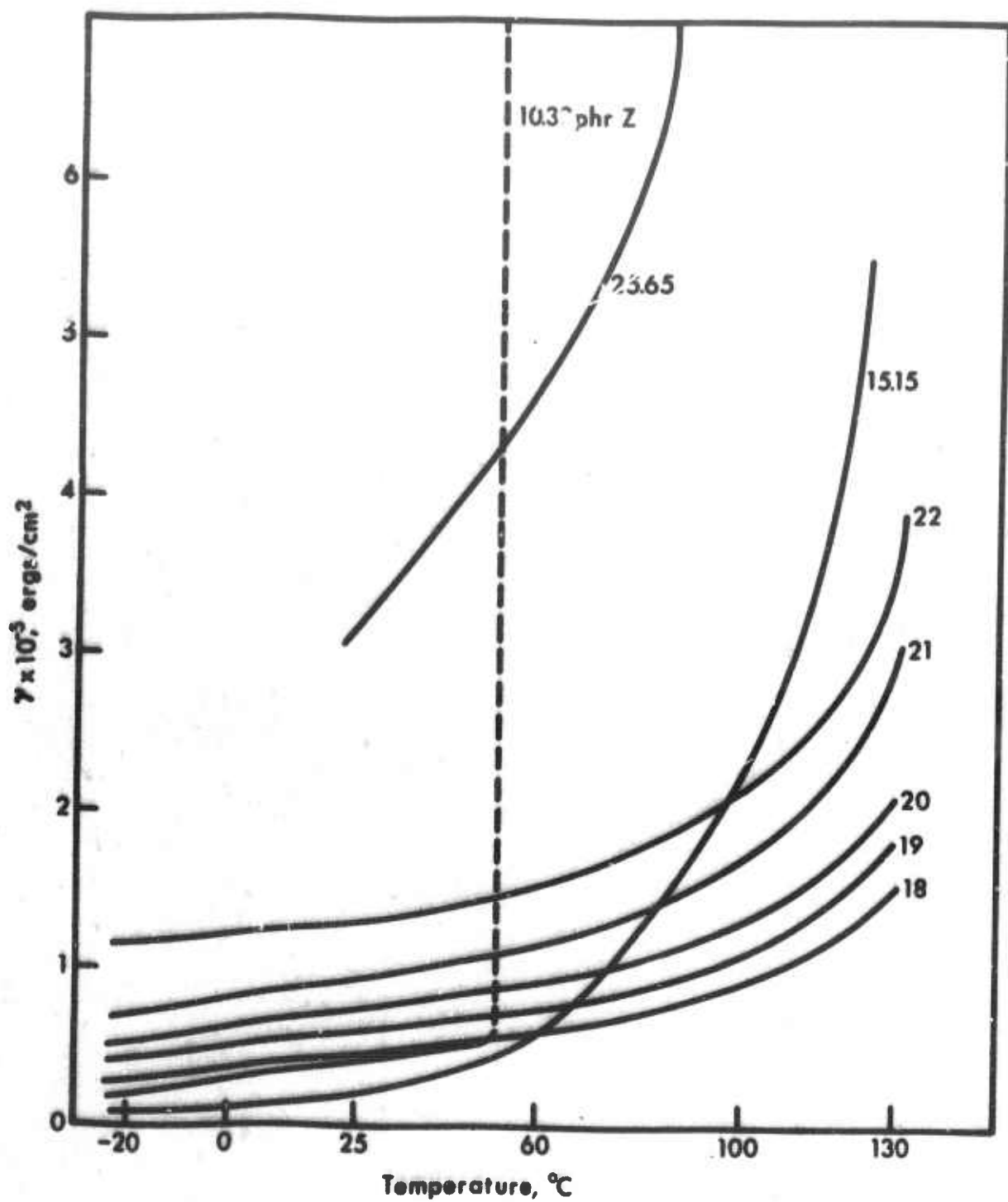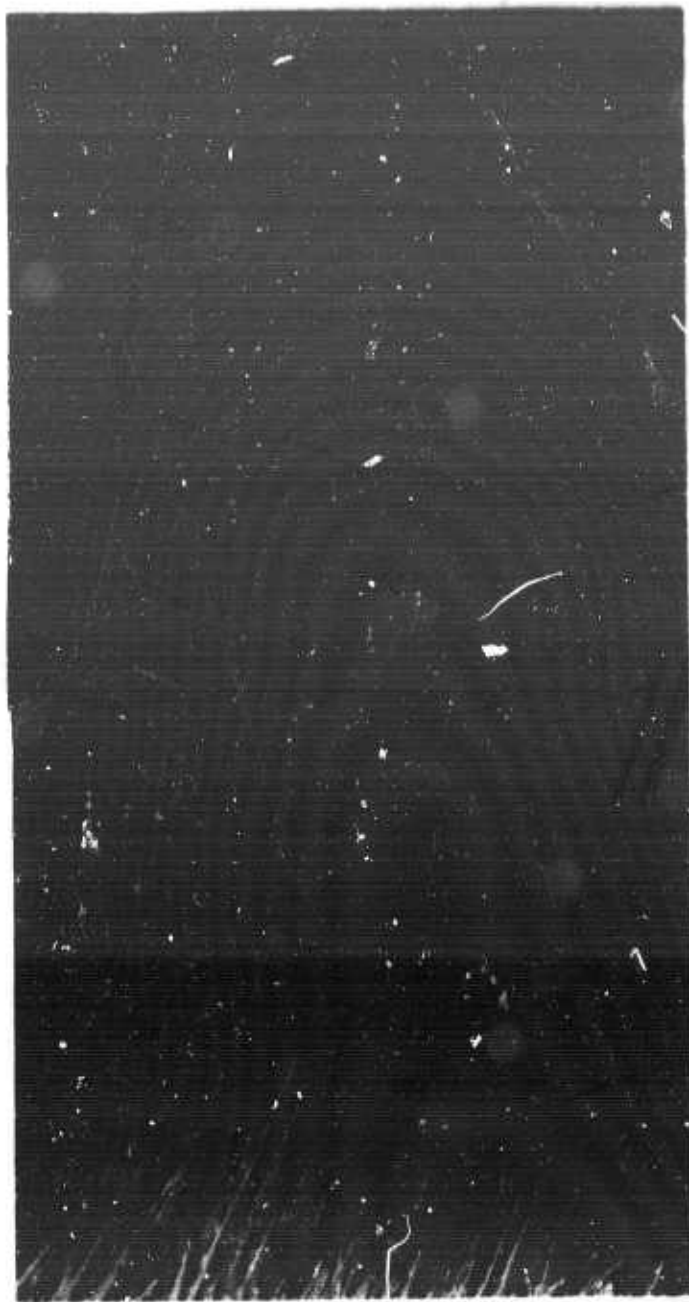| Polymer or Composite	Time in Water	% Water Absorbed	% Water per Unit Volume Polymer	% Change in γ
Epon 828 +				
18 phr Z	100 hours	0.37	0.37	+70
19 phr Z	100 hours	0.39	0.39	+67
20 phr Z	100 hours	0.39	0.39	+65
21 phr Z	100 hours	0.39	0.39	+62
22 phr Z	100 hours	0.38	0.38	+60
Epon 828 +				
20 phr Z				
untreated				
beads				
$v_f = .10$	100 hours	0.42	0.46	+57
.20	100 hours	0.39	0.49	+75
.30	100 hours	0.34	0.49	+100
.30	160 days	2.23	3.18	-7
Epon 828 +				
20 phr Z				
A-1100				
treated				
beads				
$v_f = .10$	150 hours	0.37	0.41	+40
.20	150 hours	0.31	0.39	+40
.10	160 days	1.95	2.17	+67
.20	160 days	1.58	1.98	+62
.30	160 days	1.29	1.84	+53
Epon 828 +				
20 phr Z				
A-156				
treated				
beads				
$v_f = .10$	135 days	2.01	2.23	+45
.20	135 days	1.98	2.47	-17
.30	135 days	2.05	2.93	-50
Epon 815 + 20 phr Z	100 hours	0.45	0.45	+50

LIST OF FIGURES AND TABLES.

Figure 1. Effect of Temperature and Catalyst Z Concentration on Gamma-Fracture Toughness of Unfilled Epon 828 Epoxies.

Direction of Propagation ⟶

100 microns

Figure 2. Fracture Surface of Unfilled Epon 828 Epoxy Cured with 20 pph Catalyst Z – Fractured at Room Temperature.

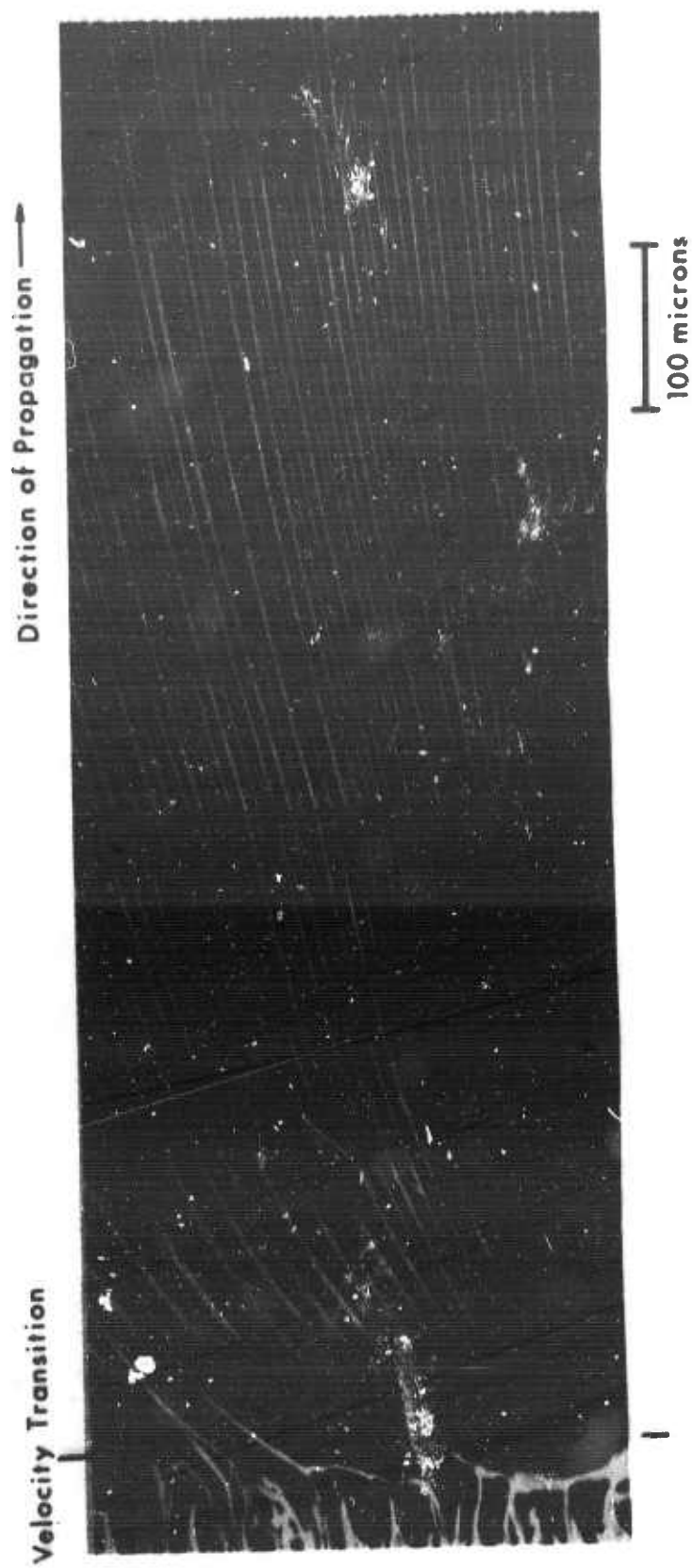Direction of Propagation →

Velocity Transition

100 microns

Figure 3. Fracture Surface of Unfilled Epon 828 Epoxy Cured with 20 PHR Catalyst Z – Fractured at 100°C.
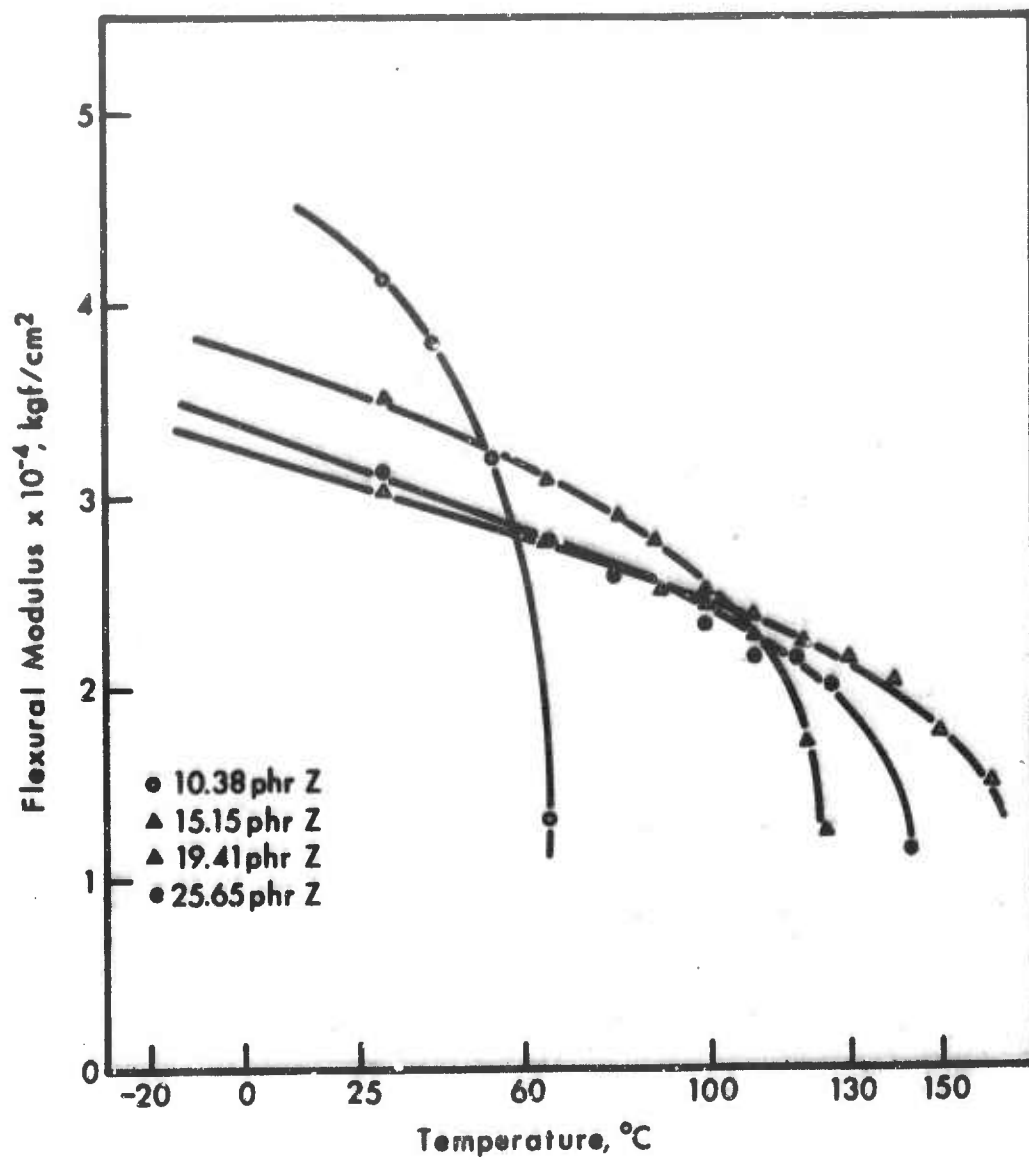
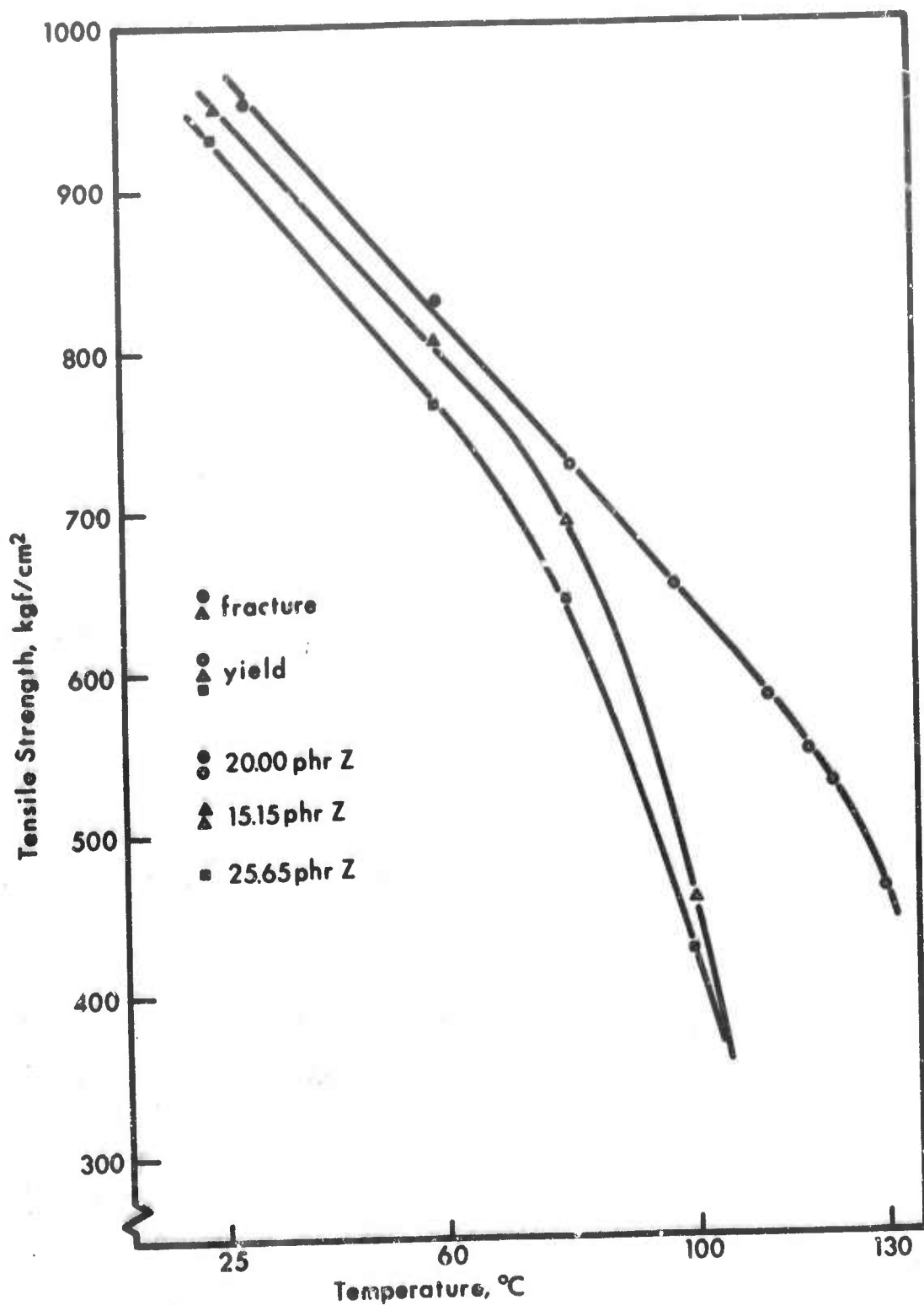Figure 4. Effect of Temperature and Catalyst Z Concentration on the Flexural Modulus of Epon 828 Epoxies.

Figure 5. Effect of Temperature and Catalyst Z Concentration on the Tensile Strength of unfilled Epon 828 Epoxies.
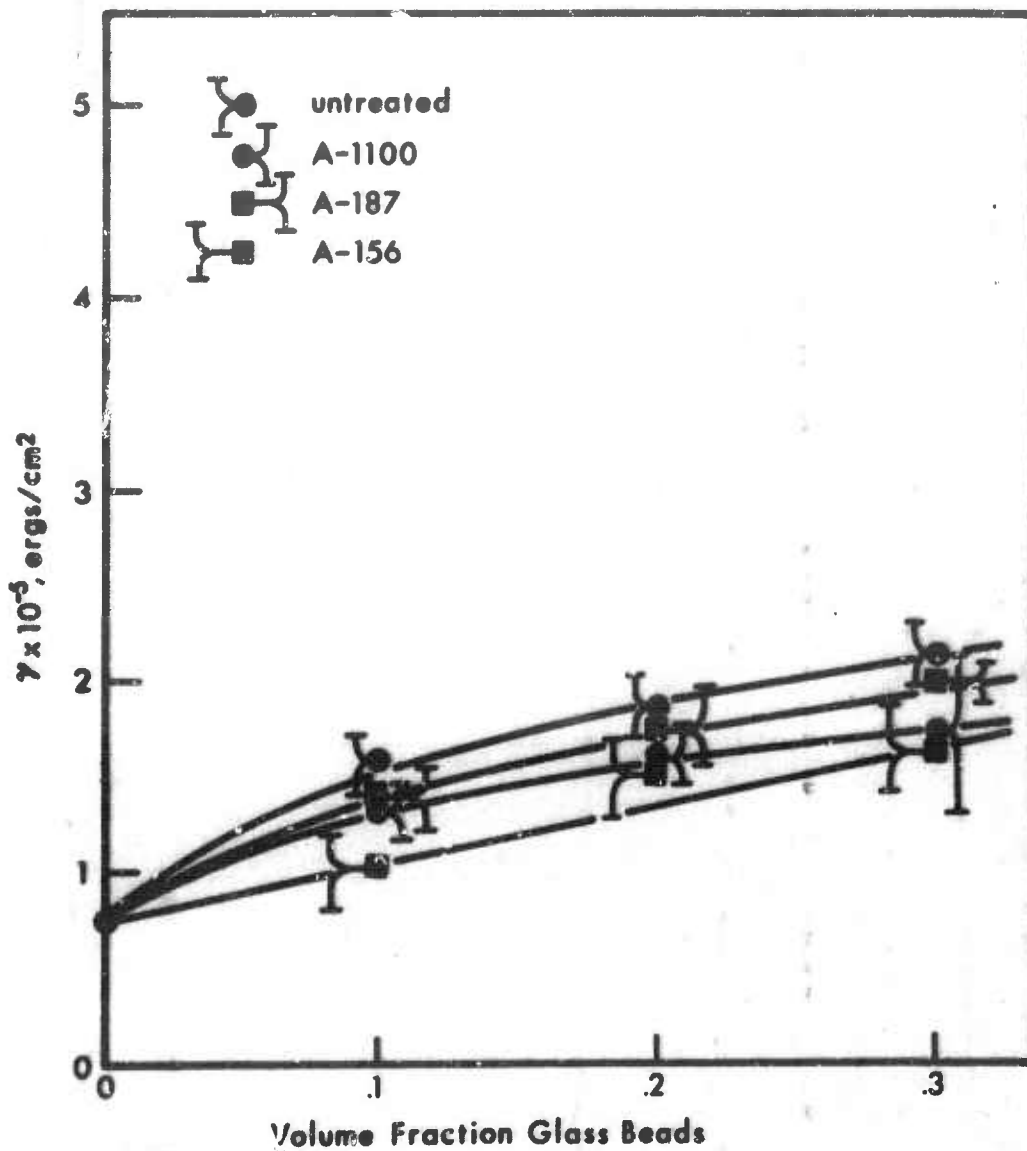
Figure 6. Effect of Volume Fraction Glass Beads and Bead Surface Treatment on the Gamma-Fracture Toughness of Epoxy Composites at 25°C.
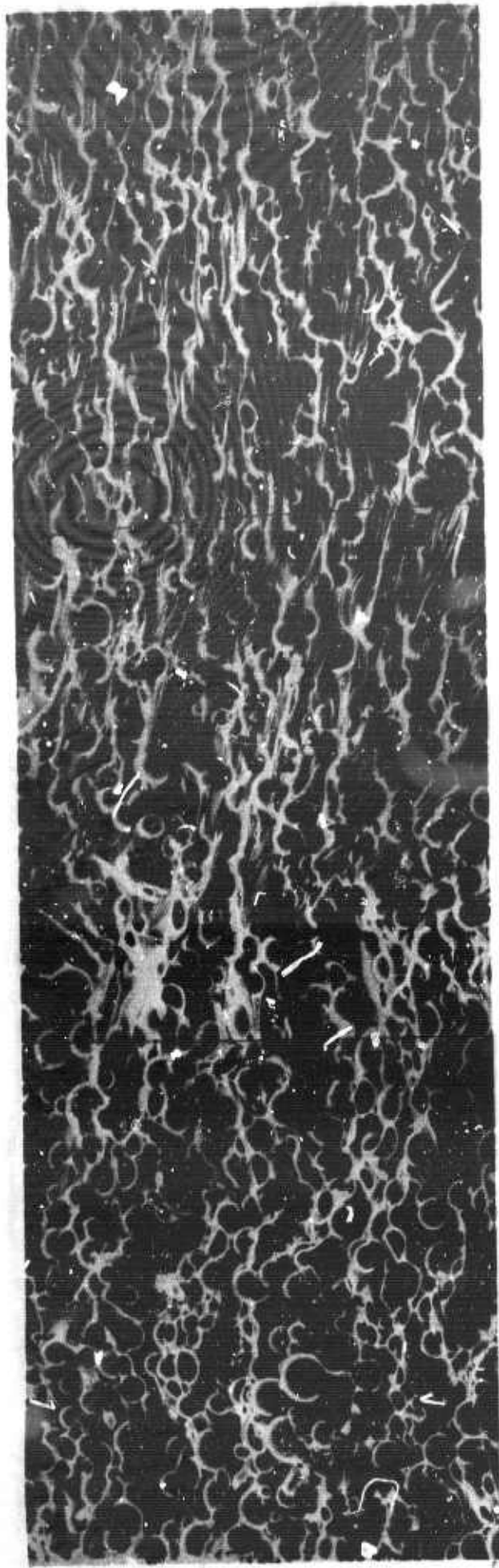
Figure 7.   Fracture Surface of 0.3 Volume Fraction A-1100 Silane Treated Glass Bead–
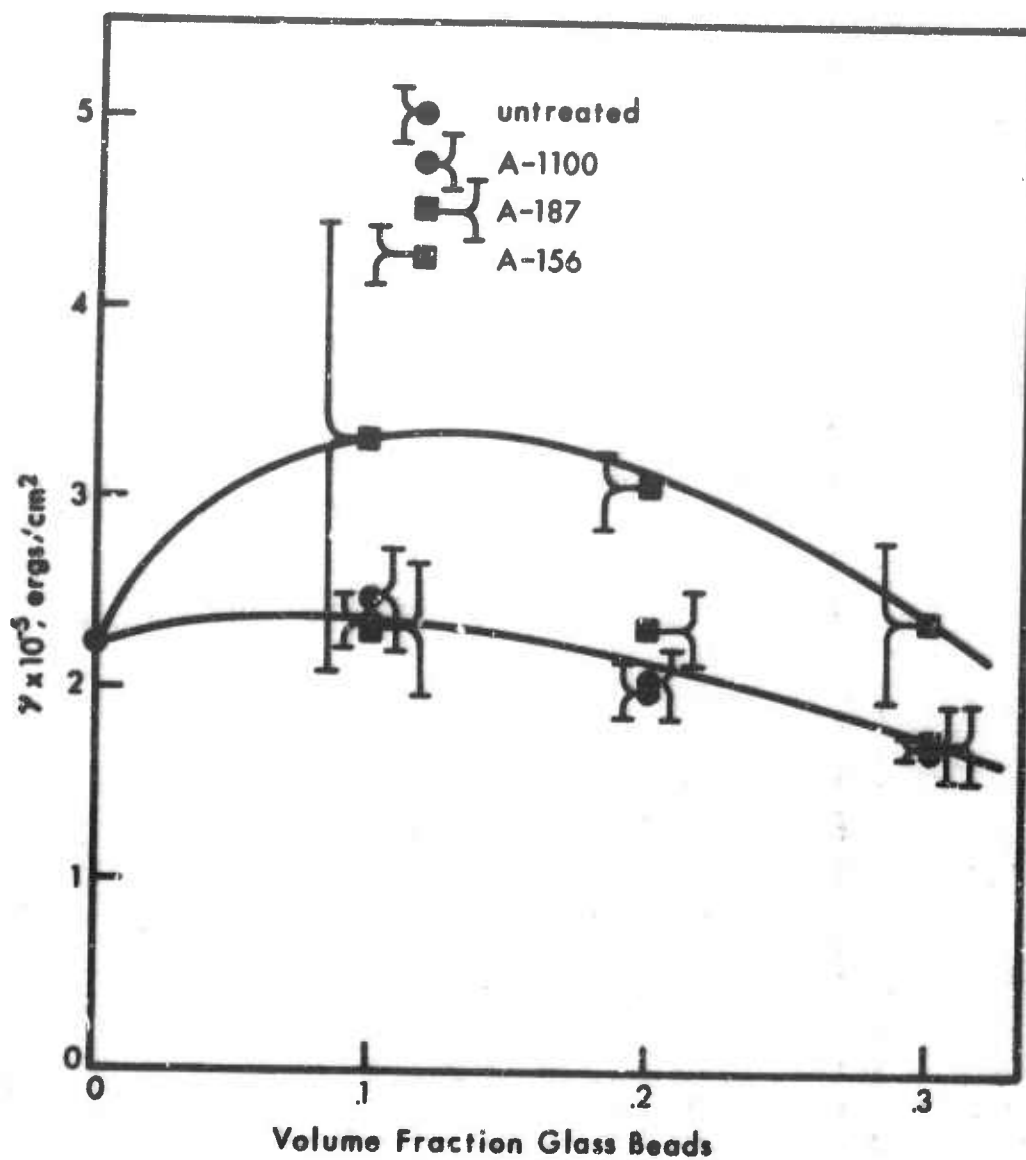Epoxy Composite – Fractured at Room Temperature.

Figure 8. Effect of Volume Fraction Glass Beads and Bead Surface Treatment on the Gamma-Fracture Toughness of Epoxy Composites at 130°C.
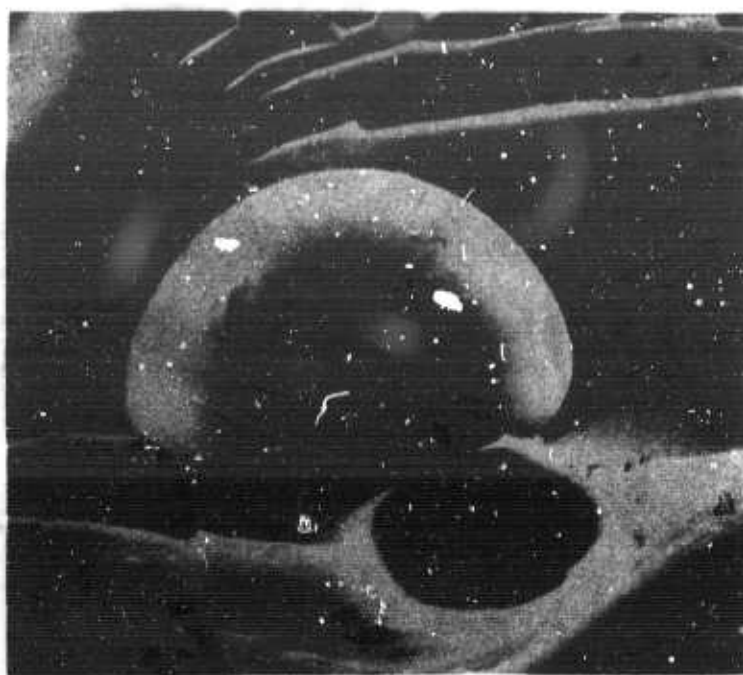
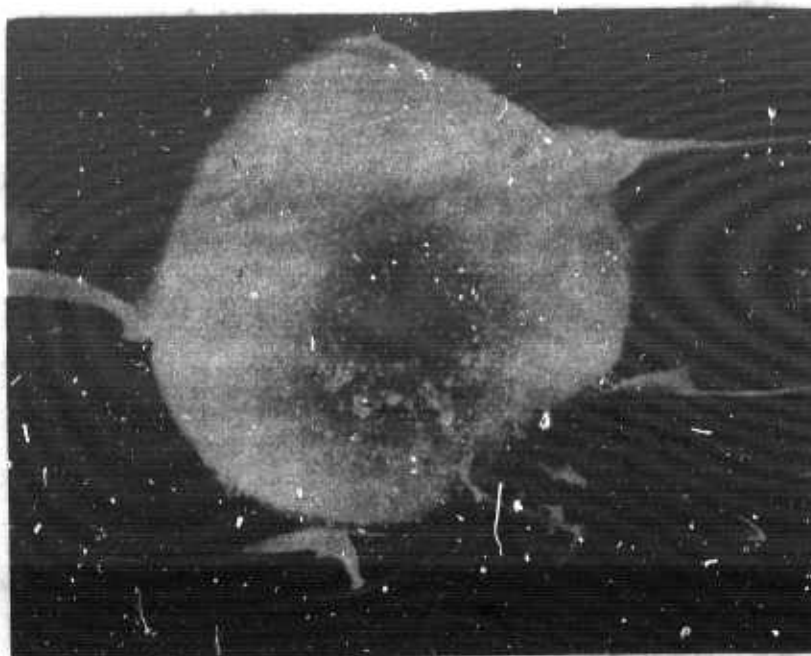Figure 9.   Fracture Surface of A-156 Silane Treated Glass-Epoxy Composite - Fractured at 100°C.

10 microns

Figure 10.   Fracture Surface of A-187 Silane Treated Glass-Epoxy Composite - Fractured at 100°C.
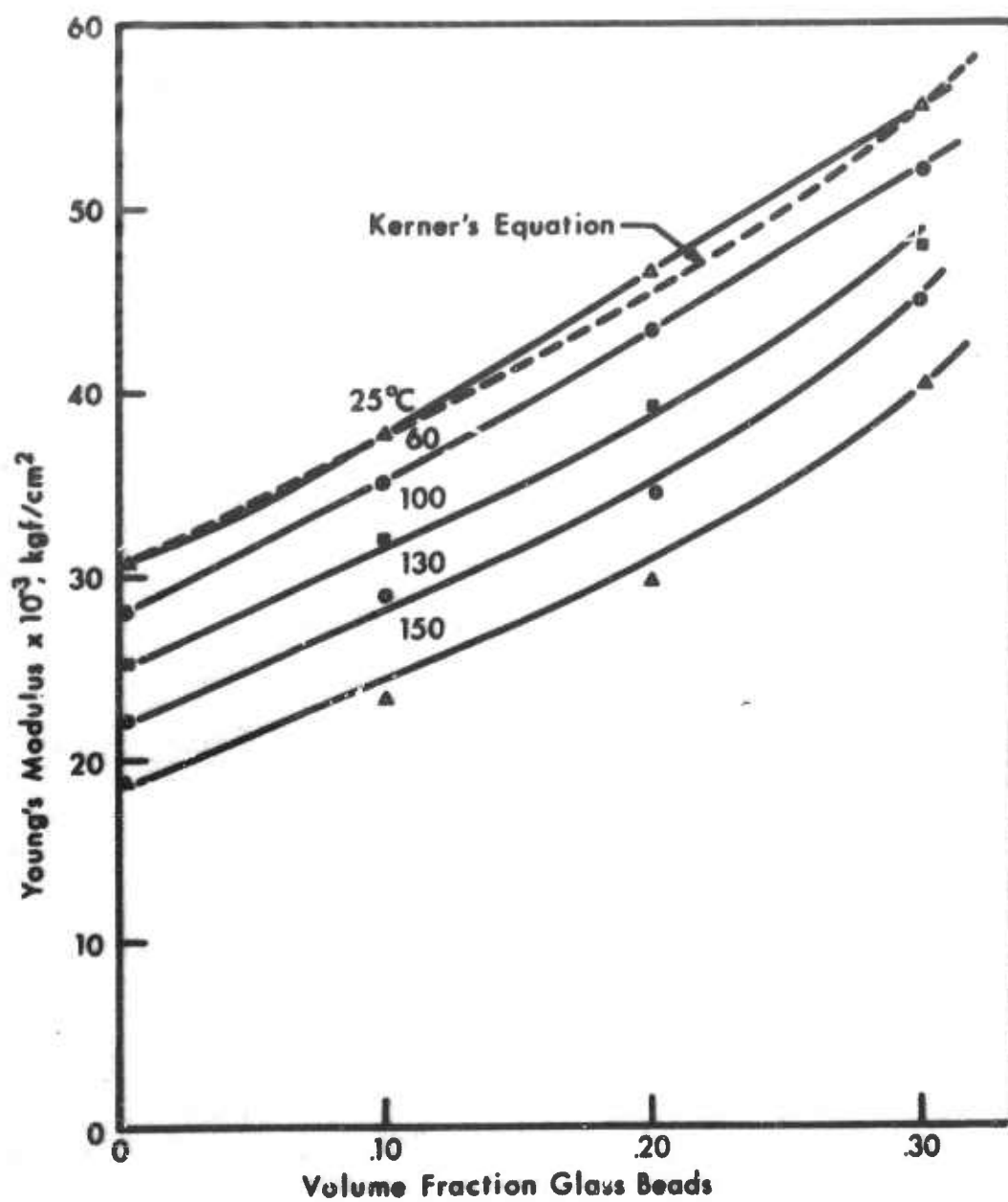
Figure II. Effect of Volume Fraction and Temperature on the Young's Modulus of Glass Bead-Epoxy Composites.
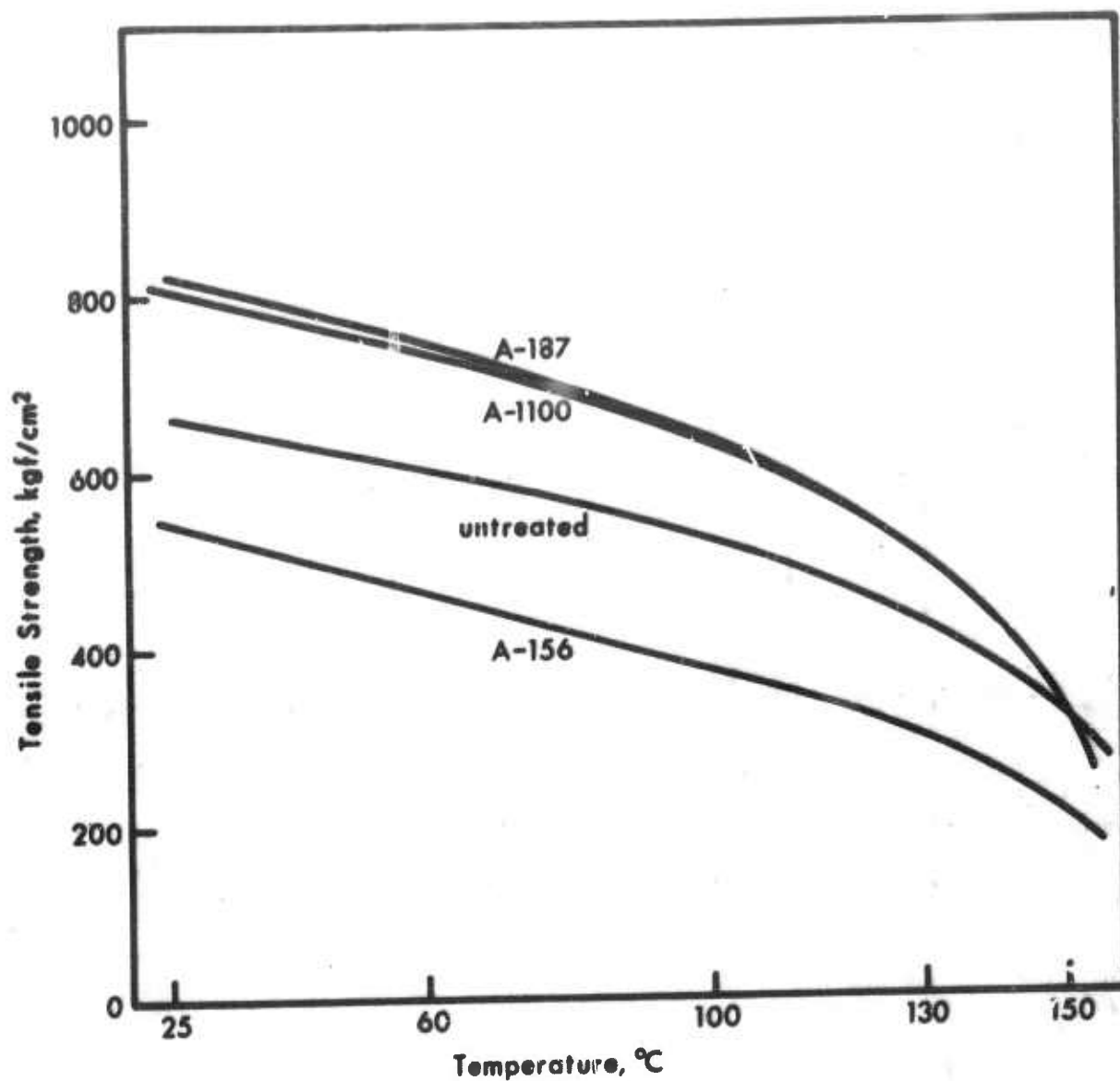
Figure 12. Effect of Temperature and Bead Treatment on the Tensile Strength of Glass Bead-Epoxy Composites.
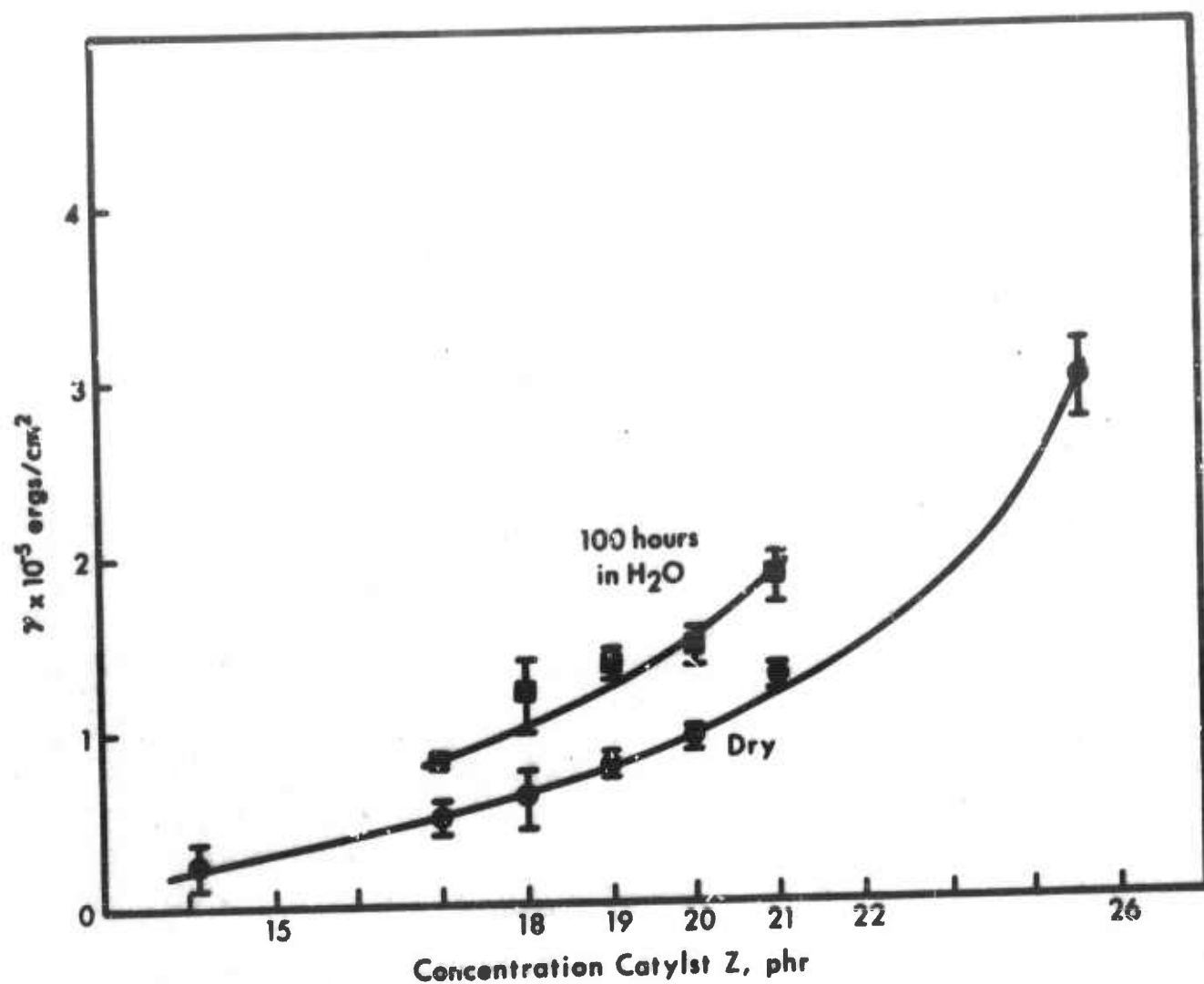
Figure 13. Effect of 100 Hours of Immersion in Water on the Gamma-Fracture Toughness for Unfilled Epon 828 Epoxies at Room Temperature.
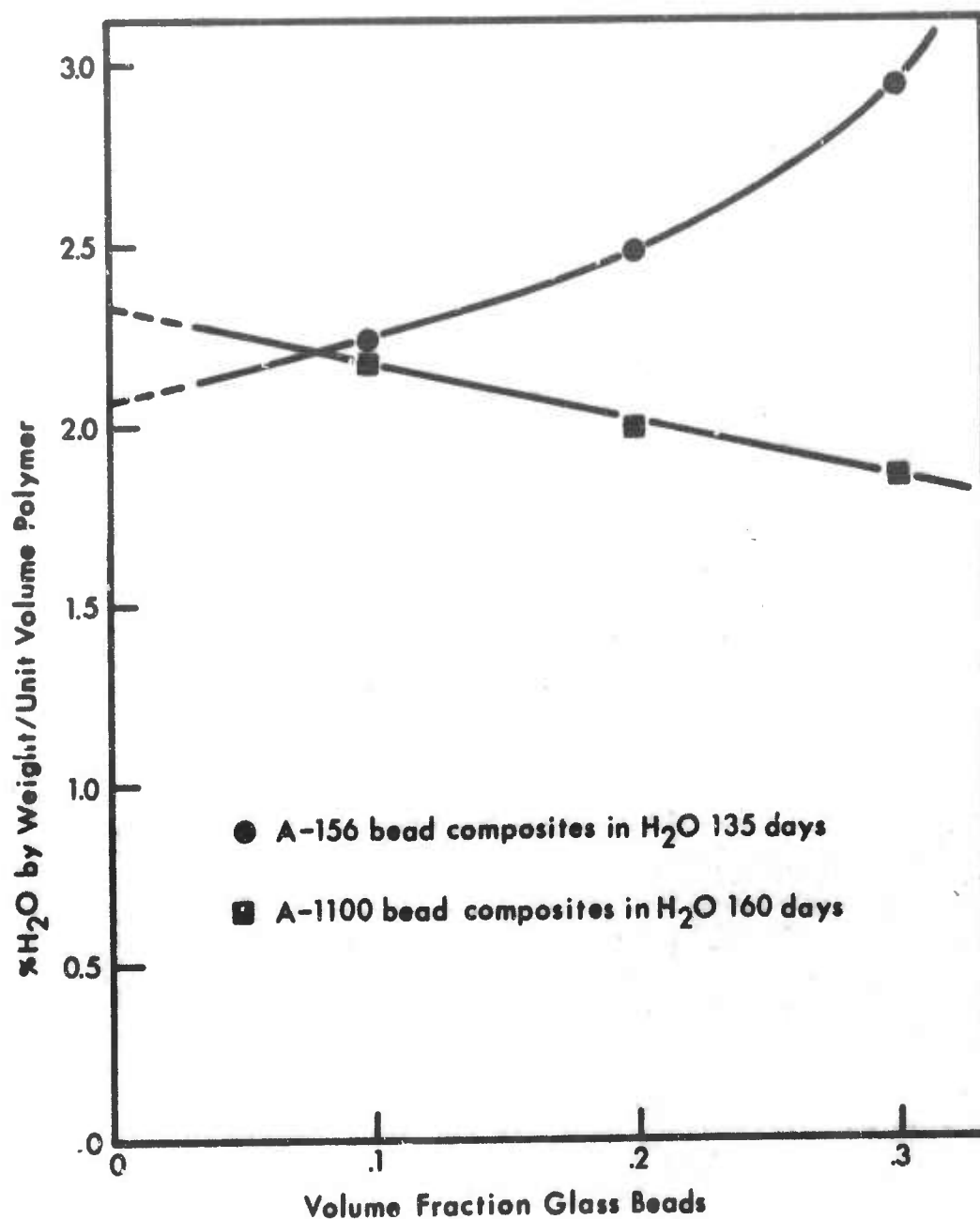
Figure 14.   Water Content Per Unit Volume Polymer as a Function of Volume Fraction Glass Beads for Glass Bead-Epoxy Composites.

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13. ABSTRACT

The plane strain fracture toughness of epoxy resins and glass bead filled epoxy composites has been investigated. Primary parameters were curing agent concentration, filler concentration, adhesion of filler to polymer, temperature, and water immersion. Fracture toughness was measured using double edge notched specimens and tensile strength and Young's modulus were measured using standard ASTM tensile bars. Scanning electron microscopy was used to examine the fracture surfaces.

It was found that the energy required for fracture depended primarily on the ability to dissipate energy in the polymer phase. At higher temperatures and/or increased catalyst concentration, the unfilled epoxy became more ductile, its fracture surface became rougher, and its fracture energy was increased. At lower temperatures, where the epoxy was relatively brittle, the addition of glass beads increased the fracture energy and induced roughness in the otherwise smooth fracture surface. When the epoxy was ductile, the addition of beads tended to decrease the fracture energy. The reduction of fracture energy for the ductile polymer was attributed to the reduction of the amount of polymer surface created.

Adhesion of the matrix to the glass beads was only important when the polymer was ductile. Improved adhesion permitted the beads to

(continued)

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
fracture toughness						
epoxy glass composites						
mechanical properties of composites						
water absorption in composites						
effects of adhesion on composite properties						

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constrain polymer flow and decrease the fracture energy. Poor adhesion permitted flow around the beads which required additional energy for crack propagation. At low temperatures, where the matrix was brittle, the additional constraints caused by adhesion appeared to make little difference.

Water absorption resulted in plasticizing the polymer, destroying the polymer near the interface. Short term immersion increased the toughness because of the additional ductility. Long term immersion tended to reduce the toughness. An effective coupling agent minimized this reduction, thereby showing that improved adhesion can improve the environmental stability and extend the useful life of the material.